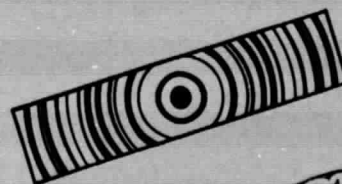
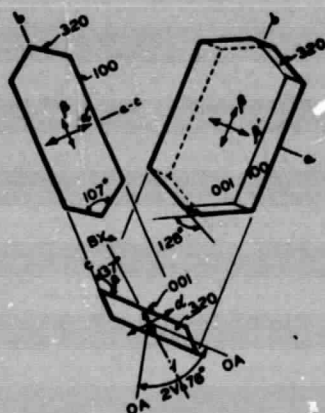
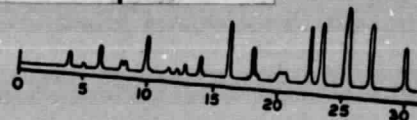
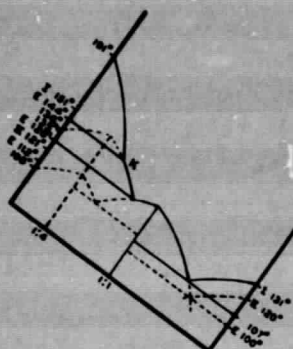
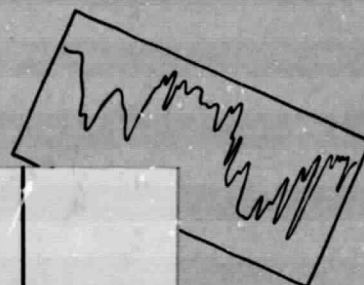
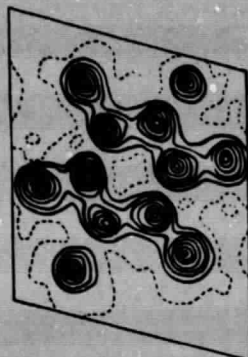


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walter c. mc crone associates, inc.



Report to
George C. Marshall Space Flight Center
NASA
Marshall Space Flight Center, Alabama 35812

Contract NAS8-29268
S/A No. 1

STUDY OF PALLADIUM
PLATING COMPONENTS

Date: 13 September 1977

MA Number: 3000

Copy 10 of 12

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This report was prepared by Walter C. McCrone Associates, Inc.
under Contract NAS8-29268 covering the Study of Palladium Plating
Components for the George C. Marshall Space Flight Center of the
National Aeronautics and Space Administration.

STUDY OF PALLADIUM PLATING COMPONENTS

At the request of Barbara R. Facemire of the Marshall Space Flight Center, Walter C. McCrone Associates has conducted a series of tests involving four solutions, four palladium deposits, three palladium electrodes, and a nickel deposit. The work was conducted under Contract NAS8-29268 with the concurrence of James A. Fountain.

Palladium deposits were prepared by electrolysis for evaluation as catalytic materials. Electrolysis was carried out in acidic solutions consisting of either 1.0 M in NaCl and 0.01 M PdCl_2 or 1.0 M NaCl and 0.04 M PdCl_2 . It was during the preparation of the palladium deposits that unexpected observations were made that led to the request for analytical services. The analyses did not, nor were they intended to, answer all of the questions. They did, however, shed light on the nature and magnitude of some of the contaminants in the solutions and in the palladium electrodes, as well as characterize the forms of the palladium deposits. Results of analyses are grouped into solution, deposit and electrode categories for comparison purposes. Tables are attached to the end of this report, as are pictures and charts.

ELECTROLYTE SOLUTIONS

Sample 1 - During electrolysis in 0.01 M PdCl_2 solution, a clear colorless layer developed at the top. Since both electrodes were Pd, it was not expected that Pd should be depleted from solution. Estimates of Pd levels in an evaporated drop of this colorless sample by electron microprobe were unsuccessful due to the overwhelming amount of Cl which has an x-ray emission energy too close to that of Pd to be distinguished from it. It was therefore necessary to resort to ion microprobe (IMA) analysis of the evaporated droplet.

A more complete description of the IMA is enclosed with this report, but it will be useful to list some of its strengths and weaknesses at this point. The IMA is sensitive to all elements and to all isotopes, but not in a single analytical run. All work reported here was carried out using oxygen as the ionizing gas, and only positive ions were detected. All metallic elements are detected but some electronegative ones, such as chlorine, are not. The response of the elements range over several orders of magnitude; gold, for example, produces a signal only 1/300,000 as strong as that of chromium. Extreme care is necessary in interpreting ion probe data.

Although only Na and Cl were detected by electron probe, IMA revealed a large number of elements at low levels (Table 1). Palladium is among those elements which was undetected supporting the contention that the loss of color is due to Pd depletion. This depletion can probably be explained in terms of a rapid migration of Pd ions towards the electrodes, and a slow diffusion of Pd ions throughout the solution. If the current is sufficiently high, Pd ions will be pulled from the more distant regions of the solution faster than they can be replaced by diffusion.

Sample 2 - The red colored solution at the anode was analyzed to determine if Pd^{+4} was present, as well as any other compounds. Previous and unrelated work, using an Electron Spectrometer for Chemical Analysis (ESCA) indicated sufficient differences in the bonding energy of Pd^{+4} and Pd^{+2} existed to distinguish between them. Although standards containing K_2PdCl_4 and K_2PdCl_6 presented no problems, diminution of the Pd signal due to excessive amounts of NaCl resulted in ESCA curves in which the Pd peaks were near background. This approach was abandoned.

Solutions of β -nitroso- α -naphthol reacts rapidly with Pd^{+2} and only slowly with Pd^{+4} to form a brown precipitate. This precipitate is soluble

in chloroform, producing a clear blue solution that appears to follow Beers Law. Photometrically measuring the Pd^{+2} concentration by comparing the color to that of a series of standards, we were able to determine the Pd^{+2} level. By analyzing the solution after reduction of Pd^{+4} to Pd^{+2} with acidic SnCl_2 we obtained a value for total Pd. The difference, then, is the concentration of Pd^{+4} . Results of analysis indicate no Pd^{+4} is present with a possible error of $\pm 10\%$. Ion microprobe data (Table 1) is similar to that of #1 with the exception of nitrogen which is much higher in 2 than 1. Nitrogen, however, is indistinguishable from CH_2 of organic compounds.

Sample 3 - A fine reddish precipitate that was discharged at the anode was analyzed by EMP and found to contain major quantities of silicon, chlorine, palladium and iron with small amounts of sodium, aluminum and chromium. The precipitate is not homogeneous, however, because it was possible to isolate some discrete particles of relatively pure material. Figures 1 and 2 show the average composition and the composition of a single particle respectively. Figure 2 has been identified as rust.

IMA of the particle-free solution shows higher levels of most of the trace elements found in 1 and 2.

Sample 4 - A droplet of the original plating of solution #4 was analyzed by IMA. Although a large number of trace elements were found, their combined concentration amounted to less than 1%.

Summary of Samples 1-4 - Sample 1 is unique among the 4 in that it contains no palladium. Sample 2 was analyzed for Pd^{+4} but palladium was found only in the +2 oxidation state. The precipitate in Sample 3 contains considerable quantities of rust and other insoluble deposits consisting of silicon, chlorine, palladium, aluminum and chromium.

Solutions from Samples 1-4 contain trace quantities of many elements including Al, Si, Ca, Cr, Fe and Ni. In general, the relative quantities of these substances increase slightly from 1 to 3, but 4, the unused electrolyte has the least.

A pattern of peaks at mass numbers 36, 62, 81 and 83, appears in all four liquids (see Fig. 3). Mass 81 is the second most intense (to Na) in Samples 1 and 2, but drops in 3 and is lowest in 4. We have no clue to the identity of the substance or substances responsible, but suspect it may be present in some latent form in the fresh solutions and increases in concentration as electrolysis proceeds.

PALLADIUM AND NICKEL DEPOSITS

Samples 5-8 are precipitated palladium and 14 is precipitated nickel. The grain structure of these samples was too fine to be resolved by the light microscope, and in order to have some basis for comparison, it was necessary to employ the scanning electron microscope.

At 2000X, gross differences can be seen in the structure of different granules, and even on different parts of the same granule. Some are delicate, highly defined dendrites, and others are botryoidal (see Figs. 4 and 5). Samples 5, 6 and 7 have a 1:1 ratio of dendrite to botryoid, and Sample 8 is mostly botryoidal with some very small particles.

In an effort to determine if the differences in morphology were related to the presence of one or more trace constituents, Sample 8, having almost no dendrites and Sample 5, having about 1/2 dendrites were analyzed comparatively by ion probe. Results of these analyses, presented in Table 1, show traces of Na, Al and Ca in both samples. Sample 5 contains Ni, Si, K (and possibly Mg) which are absent in 8, and a higher level of Fe. Due to the low levels of these elements, and the number of variables involved, we cannot be sure which, if any, of these elements influences the form of the precipitate.

Sample 14 is uniform, and botryoidal rather than dendritic. Electron microprobe analysis did not reveal any contamination although the sensitivity for them would be in the order of 0.1-0.3% for each element. Ion microprobe analysis was not attempted due to the lack of a reference.

PALLADIUM ELECTRODES

Samples 9, 10 and 11 were analyzed by ion microprobe after electron probe analysis showed only Pd. Analyses were made at the surface, 1 μm and at the interior. Results are presented in Table 2.

With few exceptions, the interior of the bars show only trace levels of contaminants with no observable patterns. The surface and 1 μm depth analyses are difficult to interpret; the 1 μm depth being generally more highly contaminated than the surface. We do not know why, but suggest that maybe the surface contaminants have been washed free when the sample was prepared for shipment, leaving an undersurface of contaminants. Another possibility is that the surface contaminants had diffused into the sample. Locally high levels of C, Ca and Cr in 1 μm depth in #9 may be due to the small beam size of 50 μm square.

Hydrogen can be due to organic matter as well as absorbed hydrogen gas, so we cannot be sure the hydrogen values represent absorbed gas. They are certainly due to organic matter in #9 and #10 interior.

SUMMARY AND CONCLUSION

Although a considerable amount of data has been generated, the enormous analytical difficulties and the idiosyncrasies of the instruments employed, as well as their extremely high sensitivities has resulted in new questions as well as answers.

Concerning the answers: the clear colorless solution of Sample 1 is depleted of Pd, no detectable Pd^{+4} was found in #2; the precipitate in #3 is a complex mixture of contaminants including rust; Samples 1-4 contain contaminants, both organic and inorganic; but #4 is considerably cleaner; Samples 5-8 consist of Pd crystals having both botryoid and dendritic forms. There is some reason to believe the dendritic forms are purer, although this

had not been firmly established. Samples 9-11 have highly contaminant surfaces down to at least 1 μm in depth.

It appears that the ion microprobe has unearthed the most unexpected information of a general nature, although its lack of quantitation is one of its deficiencies. This blind area can probably be filled in to some extent by some other technique such as atomic absorption. Actually, lack of time and funds prevented us from checking out some of the data which was questionable, such as analyzing several areas of the same sample in order to take into account locally high levels of some elements.

Nevertheless, we feel the data generated here can be used as a starting point in planning a more comprehensive analytical program.

Respectfully submitted,



Howard J. Humecki
Senior Research Chemist

Table 1
Ion Microprobe Analysis of Samples
1, 2, 3, 4, 5 and 8 (estimated rates)

Element	1	2	3	4	5	8
Hydrogen (1)	85	44	350	—	—	—
Boron	—	—	0.28	0.009	0.21	0.61
Carbon	140	400	140	2.5	130	68
Nitrogen and CH ₂	—	7800	4700	94	2000	—
Sodium	(2)	(2)	(2)	trace	(2)	(2)
Magnesium	—	—	1.6	—	.91	—
Aluminum	1.8	4.4	17	0.031	0.43	0.83
Silicon	0.86	0.94	—	0.46	0.25	—
Potassium	(2)	trace	(2)	trace	trace	—
Calcium	7.4	5.9	53	7.3	2.4	3.9
Chromium	0.0089	0.092	0.37	0.061	0.20	0.32
Titanium	—	—	0.054	—	—	—
Iron	0.15	1.2	12	0.59	13	1.3
Nickel	2.7	14	13	1.4	1.3	—
Copper (3)	4	2.3	15	0.12	0.9	—
Rhodium	—	0.025	—	—	—	—
Palladium (4)	low	100	100	100	100	100

(1) could be from hydrates and organic compounds

(2) sodium and potassium levels were too high to measure

(3) identification is questionable

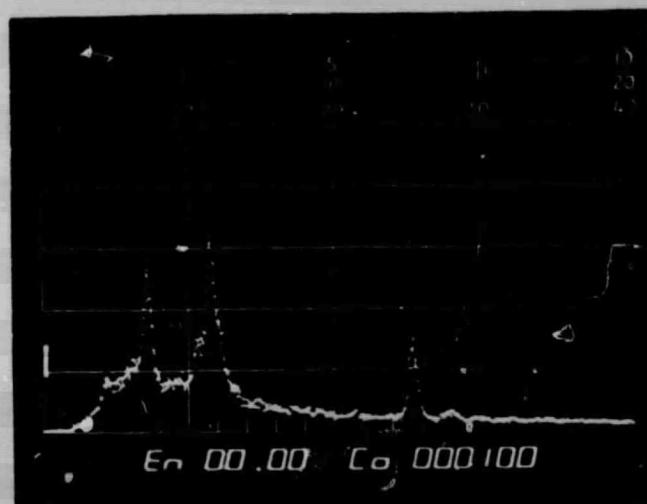
(4) all values are relative to palladium except no. 1 which had none

Table 2
Ion Microprobe Analysis of Palladium Bars, (estimated percent)

Element	Sample 9			Sample 10			Sample 11		
	Surface	1 μ m	Interior	Surface	1 μ m	Interior	Surface	1 μ m	Interior
Hydrogen	.0013	.0041	.0027	—	.0013	.0013	—	—	—
Boron	—	—	—	1.5	—	—	.60	—	.38
Carbon	—	15	2.5(?)	—	—	.8	.8	—	1.7(?)
Sodium	*	*	*	*	*	*	*	*	*
Magnesium	—	.45	—	.0035	.22	.0035	.25	.064	.012
Aluminum	.009	.43	.0054	.086	1.0	.024	.44	.20	.036
Silicon	.0017	.10	—	.23	1.6	.0025	.29	.011	.046
Calcium	.035	48(NO?)	.12	.42	.72	.04	.67	.15	.048
Chromium	.03	7.9(?)	.0023	—	.21	.0017	—	.23	—
Titanium	.019	.004	—	—	.009	.0005	.003	.0005	.001
Iron	—	.008	.008	.079	.69	.037	.15	.79	.035
Nickel	.24	—	—	.016	—	—	—	—	—
Copper	5.6(?)	—	—	.22	—	—	—	—	.087
Zirconium	—	—	.004	.002	.02	.002	.002	—	—
Rhodium	—	—	.008	.0012	—	.0012	—	.0012	—
Palladium	—	—	99+%	—	—	99+%	—	—	99+%

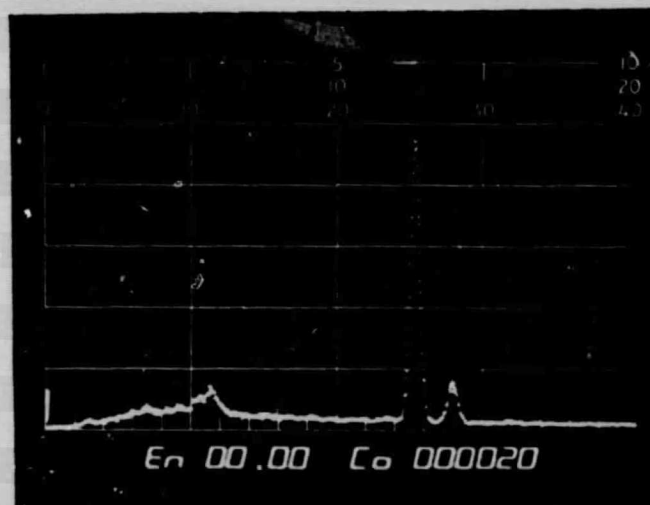
* sodium and potassium levels are too high to be measured

(?) identification is uncertain



Na Al Si Cl Pd Cr Fe

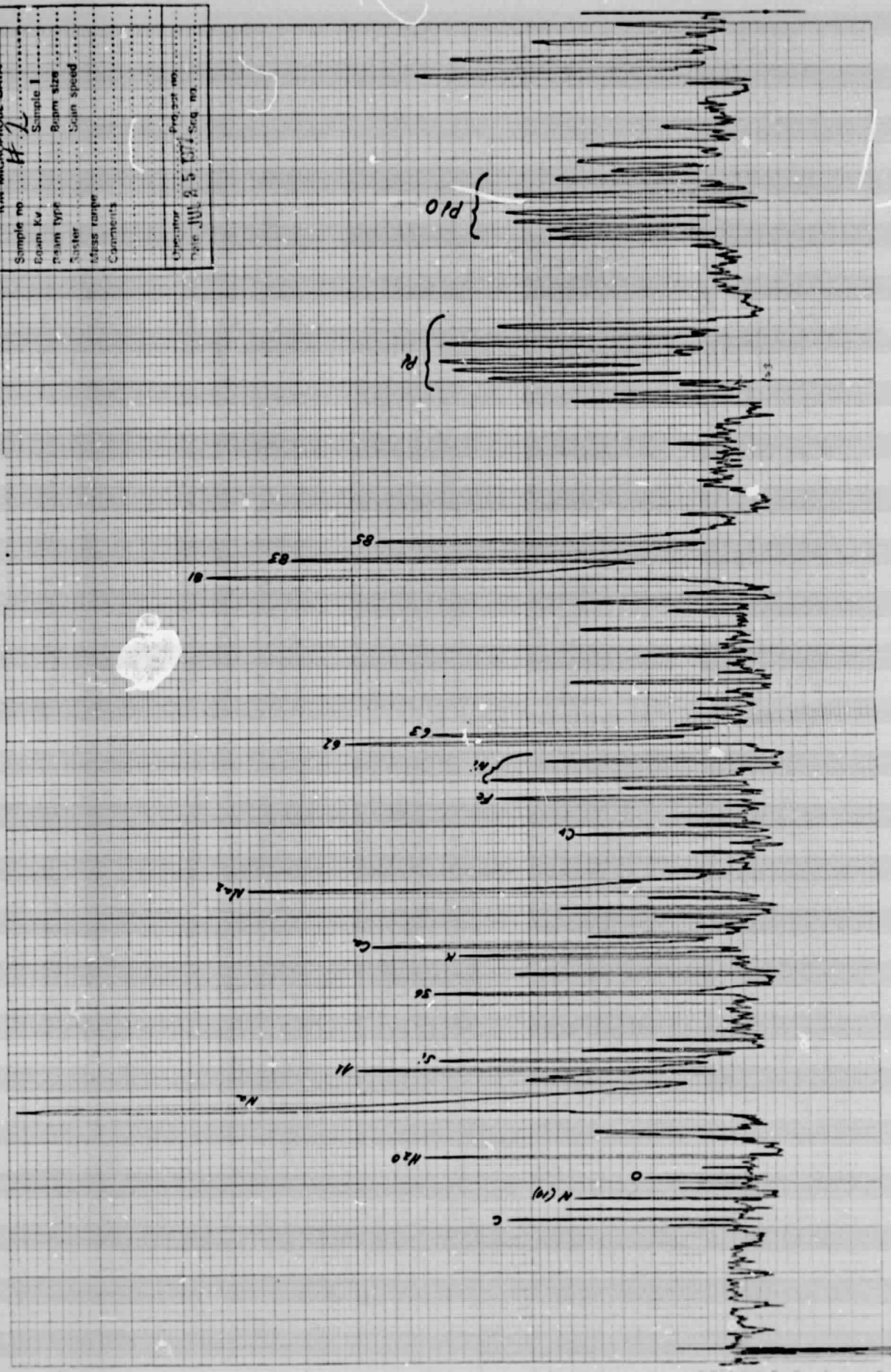
Figure 1 Energy dispersive X-ray spectrum of particles in Sample 3 - 300 μm square area



Fe Al Si S Cl Pd Fe

Figure 2 Energy dispersive X-ray spectrum of single particle isolated from Sample 3

ICM MICROPHONE DATA	
Sample no	# 2
Beam kv	Sample 1
Palm type	Beam size
Filter	Scan speed
Mass range	
Comments	
Operator	Project no.
Date	Seq. no.



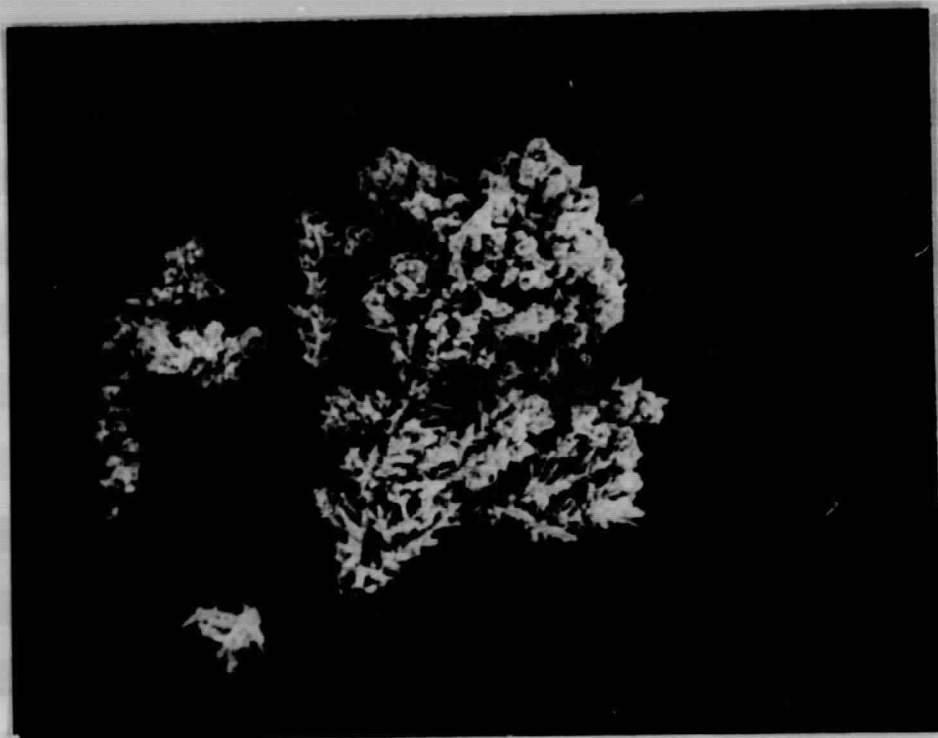


Figure 4 #5 Palladium deposit at 2000X

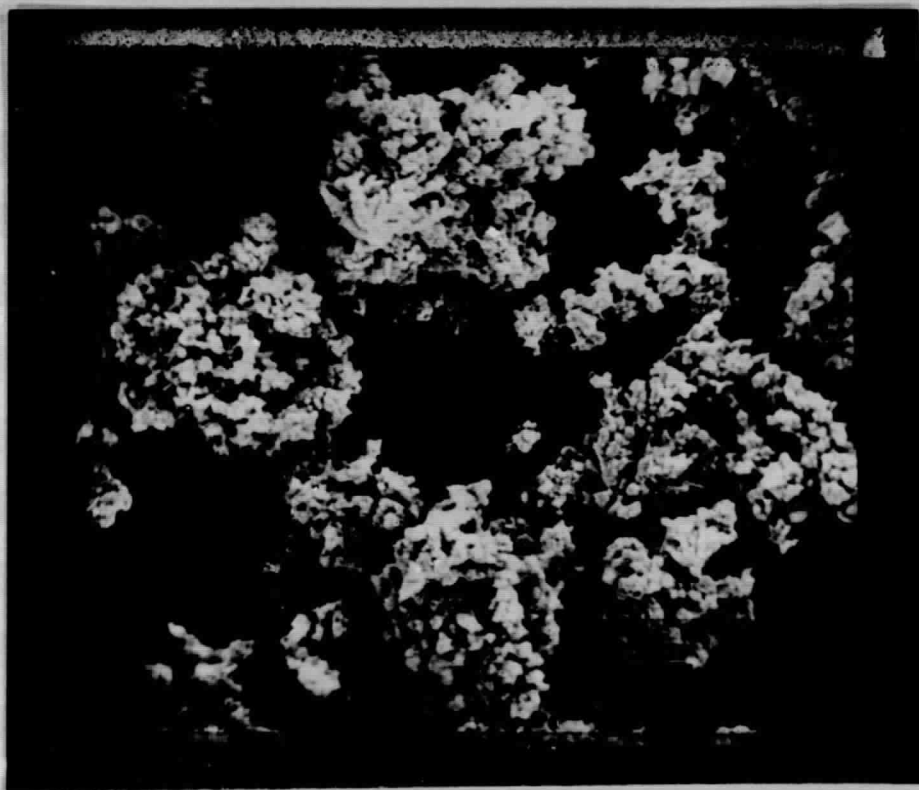


Figure 5 #8 Palladium deposit at 2000X